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DETERMINATION OF VOLATILE FATTY ACIDS IN NATURAL RUBBER LATEX

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A common method of assessing deterioration in natural rubber latex is to determine the total concentration of acidic substances by KOH titration. The method suffers from several disadvantages both as a test for decomposition and as an index of processing behaviour. It is now shown that a substantial proportion of the acids formed in latex as a result of natural degradation processess can be distilled in steam and that these volatile acids consist mainly of acetic with some formic and propionic acid. It is suggested that a test of spoilage based on the estimation of these acids would be free from the disadvantages that are inherent in the KOH titration, and a method of determining quantitatively the volatile acids in latex has been worked out accordingly.

The want of a chemical method to determine incipient decomposition in preserved latex has been long felt by producers and consumers of latex. A method often used is to neutralise the ammonia in latex with boric acid or sulphuric acid and to judge the extent of decomposition from the intensity of putrefactive odours. This method, besides having limitations common to all subjective tests, is insufficiently sensitive to detect the early stages of putrefaction.

Another way of assessing deterioration in latex is to determine the total concentration of acidic substances by KOH titration.[1] Though it is widely used in industry, the method suffers from several disadvantages both as a test for decomposition and as an index of processing behaviour. First, acids are estimated which titrate up to pH 11.2, thus failing to discriminate between stabilising (*i.e.* soap forming) and destabilising (*e.g.* formic, acetic) acids. Second, conjugate acids of bases, basic groups of zwitterions from amino acids *etc* are included. Third, it fails with latices to which soaps or fixed alkalis have been added.

Following up observations made in 1941 by the late W.S. Davey Esq at the Rubber Research Institute of Malaya we have now shown that a substantial proportion of the acids formed in latex as a result of natural degradation processes can be distilled in steam and that these volatile acids consist mainly of acetic with some formic and propionic acids. It is considered that a test of spoilage based

on the estimation of these acids would be free from the disadvantages that are inherent in the KOH titration, and methods of determining quantitatively the volatile fatty acids in latex have accordingly been worked out.

OUTLINE OF METHOD

The essential steps in the determination are to isolate the latex serum and to estimate by acidimetric titration the acids which can be distilled therefrom. Two methods of preparing the serum are described below together with two methods of distillation. To isolate the serum a neutral coagulant such as ammonium sulphate is preferred to an acid because it induces a slow, even coagulation; whereas acid coagulants may form local clots that hinder the uniform distribution of coagulant throughout the liquid phase. With salt coagulation, the yield of serum obtainable from a given sample of latex is small. It is convenient, therefore, to consider acid coagulation as the appropriate means of isolating the serum when carrying out the macro scale (constant volume) distillation procedure (*A*), and ammonium sulphate coagulation as the preferred method for the semi-micro distillation (*B*).

Of the two variants of the distillation technique the first to be described (*A*) provides a semi-quantitative estimate of the amounts of individual volatile fatty acids present in latex, while the second (*B*) serves as a rapid method for the determination of total volatile acids.

A. MACRO SCALE (CONSTANT VOLUME) DISTILLATION

This procedure is based on the Duclaux principle [2,3] that when a dilute solution of volatile substance is distilled at constant volume the amount of volatile solute passing over into the distillate is related to the volume of the distillate by

$$k = \frac{1}{v} \ln \frac{a}{a-x} \quad \ldots\ldots\ldots [1]$$

where a is the amount of solute originally present in the distillation flask, x is the amount that passes over into volume v of distillate, and k is a constant characteristic of the volatile substance. Transposed into exponential form this equation may be written,

$$x = qa \quad \ldots\ldots\ldots [2]$$

$$\text{where } q = 1-\exp(-kv).$$

Experiment has shown that the distillation constant k (and hence the coefficient q) is not wholly independent of the dimensions of the apparatus and the conditions of the distillation; nevertheless consistent and reproducible results can be obtained if the apparatus is not varied and the procedure is adequately controlled.

If the volatile acids of latex consisted exclusively of

one individual, say acetic acid, it would be possible to estimate a from equation [2] by simply titrating a given volume of distillate, having first determined q from a preliminary experiment with a known solution of acetic acid. Distillation and chromatographic evidence show, however, that in latex we have a mixture of formic, acetic and propionic acids each of which will distil independently in accordance with an equation of the form of [2]. Thus if F, A & P are respectively the amounts of formic, acetic and propionic acid initially present in the distillation flask the total amount of mixed acids that will pass over into a distillate of volume v will have a titre value,

$$t_1 = p_1F + q_1A + r_1P \quad \ldots\ldots [3]$$

where p_1 q_1 r_1 are the coefficients corresponding to formic, acetic and propionic acids respectively, and to a distillate of volume v_1.

In equation [3] coefficients p_1 q_1 r_1 can be predetermined by separately distilling at constant volume known solutions of formic, acetic and propionic acids, while p_1F, the amount of formic acid in the distillate, can be found by any of the specific methods available for the determination of formic acid. To evaluate the remaining unknowns A & P we require one more equation and this may be obtained by collecting and titrating a further volume v_2 of distillate immediately after the first volume v_1. If p_2 q_2 r_2 are the coefficients, previously determined, corresponding to the combined volume $(v_1 + v_2)$ of the two distillates and t_2 is the titre value of the second distillate,

$$t_1 + t_2 = p_2F + q_2A + r_2P \quad \ldots\ldots [4]$$

Subtracting [3],

$$t_2 = (p_2 - p_1)F + (q_2 - q_1)A + (r_2 - r_1)P. \quad \ldots [5]$$

From equations [3] and [5] it follows that if the solution being distilled contained only one volatile acid the ratio of the amounts passing into two successive distillates would be a function only of the volumes of distillate and of the distillation characteristics of the acid. Thus the ratio of the titres of two successive distillates serves to characterise the substance being distilled from a single component solution and often provides a useful indication of the main constituents of a mixture of which the precise composition is not known.

TABLE I: AMOUNT CARRIED OVER INTO DISTILLATE, AS FRACTION OF AMOUNT INITIALLY IN DISTILLATION FLASK

Volume of distillate	*Titre*	*Formic*	*Acetic*	*Propionic*
50 *ml*	t_{50}	0.091	0.166	0.292
200 *ml*	t_{200}	0.261	0.409	0.495
	t_{200}/t_{50}	2.87	2.46	1.69

To illustrate these relationships TABLE I shows results that were actually obtained by separately distilling 0.01 N formic, acetic and propionic acids at constant volume and determining the quantity of acid that passed over into (*a*) the first 50 ml and (*b*) the next 200 ml of distillate. Clearly if an unknown mixture of all three acids were distilled in the same apparatus the titre values of the successive distillates could be written

$$t_{50} = 0.091\ F + 0.166\ A + 0.292\ P$$
$$t_{200} = 0.261\ F + 0.409\ A + 0.495\ P$$

from which A and P could be calculated if formic acid in the combined distillates, *i.e.* $(0.091 + 0.261)\ F$, were separately determined.

In passing it should be noted that acetic acid is the predominating volatile acid constituent of latex (*vide infra*), formic and propionic acids being present in only small amounts. Consequently the error introduced by assuming volatile acids other than acetic to be wholly absent ($F = P = O$ in equation 3) is always small and often negligible. For practical purposes a sufficiently close estimate of the total volatile acids may usually be obtained by multiplying the acid found in a single volume of distillate by a predetermined constant factor.

In the special circumstance where a single volatile acid is present and two successive distillates each of volume v are collected and titrated, a simple expression for a the amount of acid initially in the distillation flask, can be derived from the fundamental equation [1] in terms of the amounts of acid found in the distillates. Denoting these amounts by the corresponding titre values t_1 and t_2 it can be shown that

$$a = t_1^2/t_1 - t_2$$

an expression which is independent of the distillation constant of the acid being distilled and of the volume of the two distillates, provided these are equal.

B. SEMIMICRO SCALE (TOTAL RECOVERY) DISTILLATION

Although useful for indicating the individual volatile acids present, as well as for estimating the total amount, the Duclaux distillation (*A*) is slow (about 1½ hours to distil 250 ml) and the identification of acids from distillation constants is subject to considerable uncertainty. In the routine assessment of latex spoilage, for which a knowledge of the total volatile acid content is usually sufficient, it is preferable to employ a distillation technique that effects the *total* recovery of acids accurately and rapidly. Because of the moderate volatility of the lower members of the fatty acids series their complete recovery by distillation is not easy to accomplish. Experiments with model sera show, however, that recovery becomes more complete as the scale of the distillation apparatus is reduced. Excellent results

have in practice been obtained by steam distilling in the highly efficient Markham still,[4] but no doubt other stills designed for the micro or semimicro determination of ammonia could also be used successfully.

APPARATUS AND PROCEDURE

A

For the constant volume distillation the apparatus [5] consists of a 400 ml distillation flask connected to a source of steam and an inclined Liebig condenser which leads to a graduated receiver. The distillation flask is marked to show the 150 ml level. The rate of steam supply is controlled by heating water in a 2 l Pyrex steam generating flask with immersion coils (nickel chrome *ca* 80 ohm) connected to the mains supply (230 v) through an adjustable resistance (0-40 ohm).

STANDARDISATION OF APPARATUS

Add 150 ml 0.01N formic acid to the distillation flask and steam distil, keeping the volume constant at 150 ml and the rate of distillation about 200 ml per hour. Collect a 50 ml portion of distillate, followed immediately by a 200 ml portion, and titrate each under CO_2 free conditions with 0.01 N NaOH (phenolphthalein indicator). From the respective titres, calculate the fractions of formic acid originally in the flask that were carried over into the 50 ml and 200 ml distillates. Repeat the standardisation with acetic and propionic acids. Tabulate the results of the standardisation trial as in TABLE I.

PREPARATION OF LATEX SAMPLE

Weigh latex (50 $\pm$ 0.5 gm) of known dry rubber and total solids content in a beaker, dilute with water (100 ml), add a mixture of 5 N H_2SO_4 (20 ml) and 20% phosphotungstic acid (5 ml) to precipitate rubber and proteins. Calculate the total volume V of the aqueous phase from the d.r.c. of the latex, the specific gravity (1.02) of serum, and the volume (125 ml) of added water and coagulant. Stand for half an hour and transfer the coagulum together with its serum to a Buchner funnel fitted with filter paper. Collect as much serum as possible by pressing out the coagulum on the filter. Transfer 100 ml of the filtered serum with 50 ml of water to the distillation flask.

DISTILLATION AND TITRATION

Distil with steam, keeping the volume of liquid in the flask constant at 150 ml and the rate of distillation about 200 ml per hour. Collect the first 50 ml and the next 200 ml of distillate separately and titrate with 0.01 N NaOH (phenolphthalein indicator). Reserve the combined neutralised distillates for the determination of formic acid. Determine

the blank on 50 ml and 200 ml distillates from 150 ml of water (acidified with H_2SO_4) and correct the titre values for the respective blanks. Call the corrected titre values of the 50 ml and 200 ml distillates t_1 and t_2 respectively (express titre values as milliequivalents of acid).

DETERMINATION OF FORMIC ACID

Any standard analytical method for formic acid may be used but the following procedure is preferred. To the combined neutralised distillates (reduced in volume to about 100 ml by evaporation) add sodium acetate—sodium chloride (10 ml solution containing 50 gm $CH_3COONa.3H_2O$ and 24 gm NaCl per litre) followed by mercuric chloride (10 ml 5% solution). If a precipitate of mercurous chloride forms (indicating the presence of formid acid) filter with suction through a sintered glass crucible (porosity No. 3). Wash the precipitate first with water and finally with alcohol. Dry for half an hour at 100°C, cool and weigh.

1 gm Hg_2Cl_2 = 0.0975 gm or 2.12 meq formic acid

CALCULATION

Using the constants given in TABLE I for purposes of illustration (the analyst should use the constants obtained in the standardisation of his own apparatus) we first determine F, the quantity in milliequivalents of formic acid initially present in the distillation flask, from F = (meq formic acid found in combined distillates)/0.352. We then write down equations corresponding to the following, and solve for A & P:

$$t_{50} = 0.091\ F + 0.166\ A + 0.292\ P$$
$$t_{200} = 0.261\ F + 0.409\ A + 0.495\ P$$

Out of the V ml of total water phase associated with 50 gm of latex, 100 ml was placed in the distillation flask. Hence the quantity of volatile acids in the latex expressed as milliequivalents of total volatile acids per 100 gm of latex is

$$\frac{2V\ (F + A + P)}{100}\ \text{meq/100 gm latex.}$$

The volatile fatty acids are usually reported as gm KOH per 100 gm total solids (VFA No.), in conformity with the conventional practice of reporting KOH No. in these terms.

In practice it frequently happens that the ratio of the two titres (t_{200}/t_{50}) is found to approximate to the ratio that is characteristic of acetic acid (*i.e.* 2.46 for the particular distillation conditions of the illustrative experiment recorded in TABLE I); it may then be sufficiently accurate to assume that the volatile acid consists exclusively of acetic acid. The determination of formic acid is then omitted and the total volatile acid, as acetic acid, is calculated from the combined titres and the predetermined constant (p_{250})

for acetic acid (0.575 in the illustration), thus

$$t_{50} + t_{200} = q_{250}A$$

This modification in the procedure can be further simplified, if desired, by making the two successive distillates equal in volume (say 50 ml). A knowledge of the distillation constant can then be dispensed with, the titre value of the acid initially present in the flask being given by $t_1^2 / t_1 - t_2$ where t_1 and t_2 are respectively the titre values of the first and second equal distillates.

By sacrificing a certain degree of accuracy the determination can be speeded by simply titrating the first 50 ml of distillate and multiplying the titre by a constant factor ($1/q_{50}$) to obtain the titre of the volatile acids originally present in the flask, assuming them to consist exclusively of acetic acid. The appropriate factor is found for a particular apparatus and set of conditions by distilling a known solution of acetic acid or, better, by deriving it from the constant volume distillation data of a number of typical latices. Using data from 118 latex concentrates we have found a value of 6.2 for this factor. This approximate method has been found useful when a rapid estimate of VFA No. is required and a 10% uncertainty in the result can be accepted.

B

The apparatus for the semimicro scale distillation consists of a Markham still* connected to a source of steam (*Figure 1*). The still is prepared for a determination by passing steam through it for at least 0.5 hour.

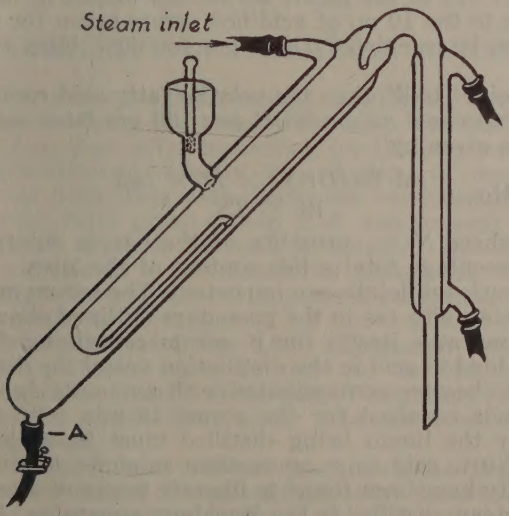

Figure 1. The Markham Still

* Manufactured by Messrs W.G. Flaig & Sons Ltd, 39 Waterloo Road, Cricklewood, London NW 2

PREPARATION OF LATEX SAMPLE

To latex (50 ± 0.5 gm of known d.r.c. and total solids content add 70% saturated ammonium sulphate solution (50 ml) in a beaker and swirl while warming over a water bath until it thickens and coagulates (generally 0.5 to 5 minutes). Press out serum by kneading the coagulum with a glass pestle and filter through a dry filter. Pipette 25 ml of the filtered serum into a dry 50 ml conical flask, acidify with 10 N H_2SO_4 (5 ml) and take one-third aliquot (10 ml) of the acidified serum for the distillation.

DISTILLATION AND TITRATION

With steam passing through the outer jacket of the distillation apparatus (steam outlet cock A open) introduce by pipette the acidified serum together with one drop of silicone anti-foam agent into the inner tube. Place a 100 ml conical flask under the tip of the condenser to receive the distillate. Partially close cock A to divert steam into the inner tube. Pass steam gently at first; then fully close cock A and adjust the rate of steam entry to give a distillation rate of 5 to 6 ml per minute. Distil for 10 minutes (*i.e.* until about 50 ml of distillate has been collected) and, after changing the receiver, for a further 5 minutes (as a check on the completeness of the distillation). Aerate the distillates with CO_2 free air and titrate with 0.01 N baryta using brom-thymol blue as indicator.

CALCULATION

From the predetermined d.r.c. of the latex and the specific gravity (1.02) of the native serum the weight of latex corresponding to the 10 ml of acidified serum taken for the distillation can be calculated (*ca* 6 gm for 60% latex concentrate).

If this weight is W, then the volatile fatty acid content of the latex expressed as gm KOH per 100 gm latex solids (VFA No.) is given by

$$\text{VFA No.} = \frac{\text{ml Ba(OH)} \times N \times 561}{W \times TS}$$

where N = normality of the baryta solution, and TS = percentage total solids content of the latex.

Two operational details are important. The serum must be acidified externally (as in the procedure outlined above), not in the apparatus itself; for if serum containing free ammonia is added to acid in the distillation vessel the distillate is liable to become contaminated with ammonia during the few seconds required for the serum to mix with the acid. Secondly the liquid being distilled must be at least 1.5 N in sulphuric acid since ammonium sulphate solutions of lower acidity have been found to liberate traces of ammonia on being steam distilled in the Markham apparatus. Any accidental carry over of liquid into the distillate as a result of foaming or excessive rate of steam input at the start or the distillation is revealed by the appearance of a precipi-

tate on titrating with baryta. If such an accident should occur the condenser tube must be cleaned by steaming to eliminate residual traces of mineral acid before the distillation is repeated or the next determination begun.

The precision of the method may be judged from the following estimates of VFA No. which were obtained by carrying out duplicate distillations on fourteen sera obtained by coagulating duplicate samples of seven latices:

	Coagulation I		*Coagulation II*	
Latex	*Dist. 1*	*Dist. 2*	*Dist. 1*	*Dist. 2*
A	0.232	0.230	0.190	0.191
B	0.338	0.340	0.348	0.345
C	0.215	0.208	0.188	0.212
D	0.120	0.119	0.124	0.124
E	0.157	0.157	0.157	0.159
F	0.078	0.076	0.078	0.078
G	0.017	0.017	0.020	0.022

A numerical estimate of the error of the determination is not quoted because it has been found to be markedly dependent on the level of the mean. For VFA Nos. below 0.20, however, the total standard error of sampling, coagulation and distillation, expressed as a percentage of the mean, is of the order of 10%. Since the error variance of the coagulation step exceeds that of the distillation by a factor of about 10, precision is gained chiefly by replicating at the coagulation stage. An appropriate procedure for routine work is to carry out single distillations on sera prepared from duplicate or triplicate samples of the given latex.

IDENTITY OF VOLATILE ACIDS IN LATEX

Using the constant volume distillation technique with acid serum from badly degraded latex the observed titre ratio (t_{200}/t_{50}) after correcting for the presence of formic acid (determined directly by reduction of mercuric chloride) was 2.36. This ratio could not be obtained unless an acid with ratio greater than 2.36 was present and acetic acid (ratio 2.46) is the only such acid. The data provided no evidence as to the identity of acids with lower ratio which might be present but it seemed reasonable to expect acetic acid to be accompanied by the next acid in the series *i.e.* propionic acid (ratio 1.69) and possibly butyric acid (ratio 1.05). As the observed ratio for the unknown mixture did not differ greatly from that of acetic acid any acids higher in the series than acetic acid must be present in small amount.

Additional evidence concerning the identity of the acids was obtained chromatographically. Several litres of degraded latex serum were steam distilled and the distillate, neutralised with sodium hydroxide, was evaporated to dryness. The sodium salts of the mixed volatile acids were converted to the free acids and dissolved in chloroform. The solution

was added to the top of a column composed of silica gel impregnated with brom-cresol green as described by ELSDON[6]. The column was developed with a 1% solution of butanol in chloroform. Separation into three bands occurred: the first band was eluted by 1% butanol/chloroform and was taken to be either propionic or butyric acid. The second band (believed to be acetic acid) remained at the top of the column with 1% butanol/chloroform but was eluted with 5% butanol/chloroform. A third band remained at the top of the column and was taken to be formic acid. A synthetic mixture of formic, acetic and n-butyric acids which was run at the same time behaved in the same way as the unknown except that the first band of the synthetic mixture (butyric acid) moved more rapidly than the first band of the latex acids. It was therefore concluded that the latex volatile acids consisted of a mixture of formic, acetic and propionic acids and this was subsequently confirmed by comparison with a prepared mixture of these acids.

TABLE II: APPROXIMATE COMPOSITION OF VOLATILE FATTY ACIDS IN LATEX

Latex	*Ammonia content %*	*Age of latex (days)*	*Total VFA (gm KOH/ 100 gm total solids)*	*Relative proportion (%)*		
				Formic acid	*Acetic acid*	*Propionic acid*
H	0.7	7	0.15	11	89	0
I	0.7	26	0.16	8	92	0
J	0.2	7	0.83	6	58	36
K	0.2	7	1.17	6	84	10
L	0.2	26	1.37	11	76	13

Typical values for the relative amounts of individual volatile acids in latex, estimated from constant volume distillation data, are shown in TABLE II. Although no great accuracy can be claimed for the percentage figures in the last three columns it is clear that acetic acid is the main acid constituent and that formic and propionic acids are usually present in relatively small amount.

SOURCE OF VOLATILE FATTY ACIDS IN LATEX

Field observations have shown that volatile acids are not present in freshly tapped latex; it is therefore of interest to consider what chemical or biological processes lead to their formation.

When hevea latex flows from the tree it is invaded by micro-organisms which find ample nutrients for rapid proliferation in the proteins, lipins, carbohydrates and mineral salts of the latex serum. Under normal conditions of tapping and collection the pH of the latex falls within a few

hours from about 6.8 to about 5.5 indicating a rapid accumulation of acids. If however latex is withdrawn from the tree aseptically and stored under rigorously sterile conditions the pH retains its initial value for many weeks[7]. Similarly if the freshly drawn latex is treated with a suitable bactericide the rate of auto-acidification is much reduced.

It is clear that whatever may be the precise nature of the changes that occur in latex after it leaves the tree there is a rapid formation of acids due largely to the action of micro-organisms. Bacteriological studies[8] have in fact shown that one organism (for which CORBET proposed the name Bacillus pandora) predominates in latex, and that this organism is capable of decomposing latex substances to produce acids.

The principle substrates whose decomposition leads to the formation of volatile acids (as distinct from acids of other classes also found in latex) are believed to be the carbohydrates present in the serum. The basis of this view is the experimental observation that the rate of production of volatile acids is (*1*) negligible in deammoniated latex from which serum substances have been removed by multiple creaming, (*2*) normal in the same latex reinforced with serum protein, and (*3*) much enhanced in the same latex reinforced with whole serum, glucose or quebrachitol.

The volatile acids, once formed, remain wholly associated with the serum chiefly in the form of ammonium salts; consequently they can be eliminated by repeated dilution and re-concentration of the latex. In a typical instance three creamings eliminated over 95% of the volatile acids whereas the total acids (as estimated by KOH No.) were diminished by only 60%, indicating that the non-volatile acids include some that are adsorbed at the rubber particle surface.

VFA NO. AS AN INDEX OF DECOMPOSITION

The sensitivity of the test for indicating latex decomposition may be illustrated briefly by a typical example: an inadequately preserved field latex (NH_3, 0.2%) changed during eight days storage by a factor of 2 for electrical conductivity, 3 for KOH No. and 30 for VFA No., while

TABLE III: FORMATION OF VOLATILE ACIDS IN INADEQUATELY PRESERVED LATEX

Age of latex (days)	*Inadequately preserved with NH_3 0.2%*			*Fully preserved with NH_3 0.7%*		
	VFA No.	*KOH No.*	*Conductivity*	*VFA No.*	*KOH No.*	*Conductivity*
	gm KOH/100 gm solids		*mho*	*gm KOH/100 gm solids*		*mho*
1	0.02	0.93	0.0056	0.02	0.89	0.0060
5	0.39	2.10	0.0094	0.02	0.94	0.0067
8	0.58	2.93	0.0116	0.02	0.96	0.0067

the same latex adequately preserved (NH_3, 0.7%) showed little change in these properties (TABLE III).

VOLATILE ACID FORMATION IN FIELD LATEX

Four clonal latices (Pil B84, Pil A44, Avros 152, BD 5) collected on the same day from adjacent plots were found to accumulate volatile acids at substantially the same rate, the mean VFA Nos. 2,5,8 and 11 hours after tapping being respectively 0.01, 0.02, 0.05 and 0.11. In each of the four latices spontaneous coagulation occurred when the VFA No. had attained the value 0.08 ± 0.01 and the pH was about 5.7. This rapid development of volatile acidity was however effectively arrested when preservatives were added to the latex at an early stage. In a typical experiment field preservatives were added either 1 hour or 5 hours after tapping, followed by ammonia (1.0%) at the ninth hour after tapping. TABLE IV records the VFA Nos. observed 10 and 50 days after the preparation of the latices. The practical implication of these results seems to be that early preservation is essential for the production of commercial latex of low VFA No.

TABLE IV: INFLUENCE ON VFA NO. OF TIME OF ADDITION OF LATEX PRESERVATIVE

Average results of four sets of experiments

Preservative added, hours after tapping			*VFA No. of latex after days*	
1	*5*	*9*	*10*	*50*
A,1.0%	—	—	0.02	0.03
A,0.05%	—	*A*,0.95%	0.03	0.07
—	*A*,0.05%	*A*,0.95%	0.06	0.09
—	—	*A*,1.0%	0.06	0.13
F,0.05%	—	*A*,1.0%	0.04	0.06
—	*F*,0.05%	*A*,1.0%	0.04	0.07
S,0.05%	—	*A*,1.0%	0.04	0.05
—	*F*,0.05%	*A*,1.0%	0.05	0.05

A = ammonia F = formaldehyde S = sodium pentachlorphenate

VOLATILE ACID CONTENT OF COMMERCIAL LATEX

In TABLE V the volatile fatty acid contents of 143 commercial latices of Malayan origin are set out in a group frequency table. Though the sample is not representative of Malayan production (being biased by the inclusion of an excessive number of low grade latices) it serves to show that the range of VFA Nos. that may be encountered in industrial practice is very wide. Experience so far suggests

TABLE V:
VFA NO. OF 143 COMMERCIAL CONCENTRATES TESTED IN MALAYA

VFA No.	*No. in group*
0.00 *to* 0.10	49
0.11 *to* 0.20	55
0.21 *to* 0.30	33
0.31 *to* 0.40	6
Total	143

that a well preserved commercial concentrate, when received by the user, should have a VFA No. not greater than 0.10; values much in excess of this figure generally indicate an inferior product, while VFA Nos. as low as 0.03, which are sometimes encountered, are a sign of exceptional care in preparation.

It is instructive to observe that the 143 Malayan latices of TABLE V varied less in KOH No. (that is in total acid content) than in VFA No. It seems from TABLE VI that this is because the non-volatile acids (estimated by the difference between KOH No. and VFA No.) are relatively invariable. This infers that the variability of KOH No. found among commercial latices is determined more by differences in volatile acid content than by differences in non-volatiles.

TABLE VI: VARIABILITY WITHIN A GROUP OF 143 LATEX CONCENTRATES
Total Solids 62 ± 2.5%

Property	*Range*	*Mean*	*Standard deviation*	*Coeff of variation*
				%
KOH No.	0.33 — 1.08	0.66	0.15	22.5
VFA No.	0.01 — 0.40	0.16	0.09	57.7
KOH No. —VFA No..	0.30 — 0.69	0.49	0.07	15.1

If so it would seem logical to assess the condition of preserved latex on the amount of volatile acids present rather than the estimate of total acids afforded by the KOH No.

VOLATILE ACIDS AND PROCESSING QUALITY

The behaviour of ammonia preserved latex in many manufacturing processes is well known to be influenced by the nature and amount of acidic substances present as ammonium salts or soaps. The work of WREN[9] showed that the viscosity changes of zinc oxide compounded latex (*i.e.* the stability of latex towards zinc oxide) are largely due to the presence in the latex of acids in the form of ammonium salts. These salts enable zinc to pass into solution, and to be adsorbed to the latex particles, thus giving rise to the thickening commonly experienced. Wren concluded from his studies that the variability of commercial latex is due, in part at least, to the presence of acidic subsances, and may therefore be controlled by preventing the formation of acids or by their removal. About the same time BAKER[10] drew a distinction between the ether soluble acids which are fairly constant for a given type of commercial latex, and the water soluble acids which vary considerably in amount. He quoted figures which indicated positive correlations between zinc oxide stability and water soluble

acid content of a group of latices. Recently CASSAGNE[11] compared the heat coagulating power of a series of zinc ammonium complexes and showed that zinc ammonium formate and acetate (assumed to be formed in zinc oxide compounded latex containing ammonium formate and acetate) are particularly strong latex coagulants.

Since Baker's water soluble acids include acetic acid, the question naturally arises whether the observed large differences in volatile fatty acid (mainly acetic acid) content are reflected in the processing behaviour of commercial latex. To this question there is at present no answer because the determination of volatile acids is not yet common practice among latex users and the correlation of VFA No. with technological quality has not been studied. Tests made on a high grade concentrate ten days after the addition of ammonium acetate in varying amounts suggest that ammonium acetate, in concentrations in which it normally occurs in commercial latex, markedly depresses mechanical stability (TABLE VII). Parallel effects are observed in the stability of latex towards zinc oxide (TABLE VIII). There is thus good reason to expect that volatile fatty acids in latex will be found to have a technological importance *per se* in addition to their importance as a diagnostic index of decomposition.

TABLE VII: EFFECT ON MECHANICAL STABILITY TIME OF THE ADDITION OF AMMONIUM ACETATE TO 60% LATEX CONCENTRATE

Ammon. acetate added (equiv. VA No)	*Mechanical stability time (sec)*
nil	1650
0.047	1475
0.093	1300
0.186	1144
0.280	906

TABLE VIII: EFFECT ON ZINC OXIDE STABILITY OF THE ADDITION OF AMMONIUM ACETATE TO 60% LATEX CONCENTRATE

Ammon. acetate aded (equiv. VFA No.)	*60% Concentrate (sec)*	*60% Concentrate + Ammon. laurate 0.03% (sec)*
nil	118	173
0.047	107	142
0.093	100	133
0.186	83	127
0.280	77	108

Std error = ± *2.0 sec*

Stability was measured by a test in which latex of 55% total solids and 0.5 ± 0.05% ammonia content was allowed to stand for 1 hour in the presence of zinc oxide (1% by weight calculated on the total solids content) and then stirred at 14,000 r.p.m. until coagulation.

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